

OVERVIEW OF USGS-EPA PILOT RESERVOIR MONITORING PROGRAM

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In the Spring of 1999, a pilot monitoring project was initiated by Environmental Protection Agency/Office of Pesticide Programs/Office of Ground Water and Drinking Water (EPA/OPP/OGWDW) and the United States Geological Survey/ National Water Quality Assessment (USGS/NAWQA) to assess pesticide occurrence in finished drinking water and raw source water derived from reservoirs. The monitoring program was focused on reservoirs because they are considered to be vulnerable to pesticide contamination, and serve as an integrator of pesticide loading within a reservoir watershed. Thus, water systems that withdraw from reservoirs provide an ideal environment to assess the relative occurrence of pesticides in raw and finished drinking water. Key objectives of the monitoring program are to: provide data on pesticide concentrations in finished drinking water; provide a base-line monitoring data set of pesticide concentrations in a select number of reservoirs; link the occurrence of pesticides in drinking water with pesticide concentration data from source water bodies; associate pesticide concentrations in reservoirs with watershed and reservoir characteristics; provide pesticide concentration data for ecological risk assessment; and, to provide data to evaluate alternative monitoring frameworks to measure peak concentrations of pesticides and their degradates at public water systems.

Twelve drinking water supply reservoirs were selected for the pilot-monitoring program. Selection of reservoirs was based on pesticide use areas typical of regional cropping patterns and urban areas, vulnerability of the reservoir, and runoff potential of soils within the reservoir watershed. In terms of vulnerability, the selected reservoirs generally represent small reservoirs with high pesticide use areas and high runoff potential in their watersheds. The selected water sampling strategy was designed to link pesticide occurrence in finished water to occurrence in raw source water, and to link pesticide occurrence in raw source water to pesticide occurrence in the reservoir and to watershed characteristics impacting the water supply reservoirs. Thus, samples of the public water system compliance tap (finished water), the public water system intake (raw water), and the reservoir outflow (reservoir integrator) were taken at the same time for each sampling period.

The sampling frequency for each reservoir was designed to provide reliable occurrence data for estimating the annual mean and daily peak concentrations for many types of pesticides. The sampling strategy was focused around the period with the highest pesticide use. Each reservoir was sampled quarterly for one year, and biweekly for a four month period beginning with the primary pesticide application season. Four reservoirs were sampled weekly for 6 months after application in order to capture peak concentrations for short-lived compounds. Three USGS multi-residue analytical methods were used for pesticide identification and quantification. Two of these methods were implemented concurrent with final method performance testing by the USGS. Although the data from these methods are currently provisional, the pilot-monitoring program is gaining a first-of-its-kind look at approximately 184 different compounds in raw and finished water supplies. These new methods can

detect 128 different pesticides and 55 potential degradation products.

Another important aspect of the monitoring program is the collection of ancillary data for interpretation of the monitoring data and context setting. Ancillary data compiled in the monitoring program capture information on water-supply characteristics, watershed characteristics, and reservoir characteristics, and estimates of pesticide usage.

Preliminary Data from the USGS-EPA Pilot Reservoir Monitoring Program

Although the data are still being analyzed and actual pesticide concentrations are not yet available, preliminary information from USGS indicate that pesticides are being detected in raw and finished water from drinking water supply reservoirs. The occurrence of pesticides in reservoirs exhibits high spatial and temporal variability. Some of the observed variability could be attributed to seasonal weather patterns such as the extreme drought in the northeastern United States in 1999.

The preliminary results from new USGS analytical schedules indicate that 88 different analytes have been detected in reservoir raw source water. In general, analyses indicate that the high use herbicides are the most frequently detected pesticides--with atrazine, simazine, and metolachlor occurring in greater than 80 percent of all water samples. In addition, degradation products of these high use compounds are found as frequently as the parent products. Diazinon was the most frequently detected (20% of the samples) insecticide. Many pesticides were detected in less than 5% of the samples. Additionally, the environmental degradation products of oxamyl and aldicarb were also detected in raw source water from drinking water supply reservoirs.

Initial observation of pesticide removal efficiencies for conventional water treatment without activated carbon ranged from 5-10% for triazine and acetanilide herbicides, and ranged from 0-100% for other compounds. Activated carbon in the treatment train had removal efficiencies of 13-60% for triazine and acetanilide herbicides and 30-100% for other compounds. These results suggest that treatment effects on pesticide removal are highly variable. Natural degradation products of pesticides may be the predominant form of exposure for some compounds. Some of these products may still be toxic to humans while others are not expected to be toxic. Herbicide degradation products of metolachlor, acetochlor, and alachlor had higher concentrations in both raw source water and finished drinking water than the parent compound. The removal efficiency of metolachlor and acetochlor and their degradation products were low through conventional water treatment or powdered activated carbon. However, in one case, the use of granular activated carbon (GAC) removed approximately of 50-80% alachlor residues.

There is an indication from the pilot-monitoring program that water treatment processes such as disinfection can cause chemical transformation of pesticides. As a part of its quality assurance program, the USGS added a known concentration of a pesticide to selected samples of both the raw and finished water from each reservoir. The purpose of these "spiked" samples was to evaluate how well the analytical methods detected the pesticide being analyzed. In a "perfect" system, the amount of pesticide that is detected in the spiked sample should be equal to the amount of pesticide that was

added. Significant differences in these values indicate potential problems. USGS found that, for organophosphates and some other pesticides, the amount of pesticide detected in the analysis was much lower in the spiked treated-water samples compared to spiked raw-water samples. Some transformation products that would result from oxidation by chlorine (for example, oxons, sulfoxides, sulfones, and oxon-sulfones of certain organophosphates) were recovered at higher levels in the analyses than would have been expected based on the amounts that were added to the spiked treated water samples. The low or non-existent analytical recoveries of some pesticides (especially organophosphates), combined with the higher-than-expected recoveries of some of their transformation products, in spiked treated water samples may have been due to oxidation by residual chlorine in the treated water.

The potential for the formation of oxidized degradates in finished waters is further supported by two pairs of raw- and finished-water samples, with each showing malathion occurring in raw water and malaoxon in finished water. These preliminary results are consistent with other published results for diazinon in chlorinated water. The current analytical methods used in the pilot-monitoring program do not measure the diazoxon the primary degradate of diazinon. Based on the observed occurrence of organophosphorus compounds and their degradation products in the pilot-monitoring program, it appears that there is still a significant amount of research to be done on organophosphorus compounds, particularly related to pesticide transformations and the potential for degradation products to occur in treated water.

Next Steps

The USGS is continuing their analysis and interpretation of the results of the first year of the pilot reservoir monitoring study. They anticipate providing EPA with a report on their findings by the end of the year. The pilot monitoring program has been extended for a second year due to weather conditions (such as 1999's drought in parts of the country) which impacted the monitoring results.